



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 1 270 676 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:  
02.01.2003 Bulletin 2003/01

(51) Int Cl.7: C09B 45/34, C09D 11/02

(21) Application number: 02013629.7

(22) Date of filing: 19.06.2002

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR

Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 19.06.2001 JP 2001185245  
06.06.2002 JP 2002165893

(71) Applicant: MITSUBISHI CHEMICAL  
CORPORATION  
Chiyoda-ku, Tokyo 100-0005 (JP)

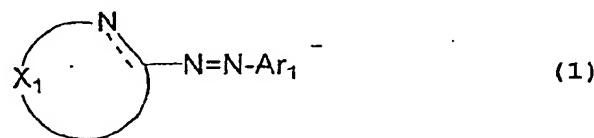
(72) Inventors:  
• Chino, Tomohiro  
Ashigarakami-gun, Kanagawa (JP)

- Yainada, Masahiro  
Aoba-ku, Yokohama-shi,  
Kanagawa 227-8502 (JP)
- Sano, Hideo  
Aoba-ku, Yokohama-shi,  
Kanagawa 227-8502 (JP)
- Shimizu, Wataru  
Aoba-ku, Yokohama-shi,  
Kanagawa 227-8502 (JP)
- Murata, Yuukichi  
Machida-shi, Tokyo (JP)

(74) Representative: VOSSIUS & PARTNER  
Siebertstrasse 4  
81675 München (DE)

(54) Metal chelated dyestuff for inkjet recording, aqueous inkjet recording liquid comprising the same and inkjet recording method using the same

(57) A metal chelated dyestuff for inkjet recording comprising a water soluble azo metal chelated compound obtainable from an azo-based compound represented by the following general formula (1)



having one or more hydrophilic groups per molecule and a metal element is described. Furthermore, an aqueous inkjet recording liquid comprising an aqueous medium and the aforementioned metal chelated dyestuff; and an inkjet recording method using the aforementioned recording liquid are described.

**BEST AVAILABLE COPY**

## Description

[0001] The present invention relates to a water soluble dyestuff for inkjet recording, an aqueous inkjet recording liquid comprising the water soluble dyestuff and an inkjet recording method using the aqueous inkjet recording liquid.

5 More particularly, the invention relates to a metal chelated dyestuff comprising a water soluble azo metal chelated compound suitable for inkjet recording, an aqueous inkjet recording liquid comprising the metal chelated dyestuff and an inkjet recording method using the aqueous inkjet recording liquid.

10 [0002] A so-called inkjet recording method which allows droplets of a recording liquid containing water soluble dyes such as direct dye and acidic dye to be ejected from a minute ejection orifice to effect recording has been put to practical use.

15 [0003] The recording liquid requires that it be fixed rapidly on recording paper widely used for general official purposes such as PPC (plain paper COPIA), paper such as electrophotographic paper and fanhold paper (continuous paper for computer, etc.) and gives a printed product having a good print quality, i.e., print having a definite contour free of running. The recording liquid further requires that it exhibits an excellent storage stability as a recording liquid. Accordingly, the solvent which can be used in the recording liquid is remarkably limited.

20 [0004] Further, the dye for recording liquid requires that it has a sufficient solubility in the solvent thus restricted and remains stable even after prolonged storage in the form of recording liquid. The dye for recording liquid also requires that it gives a printed image having a high saturation and density and an excellent water resistance, light-fastness and indoor discoloration resistance.

25 [0005] In order to form a full-color image by an inkjet recording method, inks of three primary colors, i.e., yellow (Y), magenta (M) and cyan (C) or inks of four colors, including black (Bk) added thereto, are ejected onto a recording material in a controlled amount so that these inks are mixed to form an image. In order to form such a full-color image, it is necessary to express not only a difference in color but also in color density. The dark and light colored areas are normally formed by two or more inks having different dyestuff concentrations.

30 [0006] However, the conventional inkjet recording dyestuffs are disadvantageous in that they are poor in resistance to discoloration under light, i.e., light-fastness, particularly on a light-colored area formed by an ink having a low dyestuff concentration.

35 [0007] In particular, as magenta dyestuffs to be incorporated in the recording liquid there have heretofore been used metal-free direct dyes (C. I. DR-227) or acidic dyes (C. I. AR-249), which are commercially available (The term "C. I." stands for "color index", the term "AR" stands for "acid red", and the term "DR" stands for "direct red"). However, the direct dyes have an unclear color tone. On the other hand, acidic dyes having a sharp color tone tend to have inferior light-fastness. Further, the conventional metal-containing azo-based dyestuffs have a good light-fastness but have a blurred and unclear color tone.

40 [0008] Japanese Patent Laid-Open No. 1982-42775 discloses an aqueous ink for inkjet printing comprising at least one 5-hydroxypyrazole azo dye having an azo group in the 4-position or complex salt dye thereof with copper, nickel or cobalt. Japanese Patent Laid-Open No. 1998-259331 discloses an aqueous inkjet recording liquid comprising a water soluble complex formed by a benzene azo compound and at least one metal selected from nickel, cobalt, chromium and copper. Further, Japanese Patent Laid-Open No. 1999-140367 discloses an ink composition comprising a magenta dye ligand of 4-hydroxy-3-(2'-pyridylazo)-1-(sulfo-substituted)-naphthalene having polyvalent metal ions co-ordinated therein and an ink vehicle.

45 [0009] However, these dyestuffs do not necessarily meet the requirements for sharpness of color tone, light-fastness, indoor discoloration resistance, solubility, storage stability, etc. for use in inkjet recording.

[0010] Among the metals to be incorporated in the metal chelated compound, copper is cheaper than nickel, cobalt, etc. and is desired in safety. However, any of conventional metal chelated dyestuffs for inkjet recording comprising copper incorporated therein as a metal has left something to be desired in saturation.

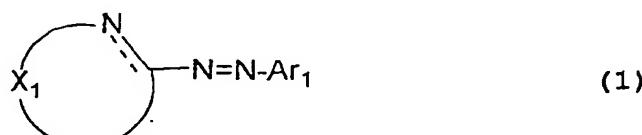
50 [0011] An aim of the invention is to provide a metal chelated dyestuff for inkjet recording which provides a recorded image having a good print quality, a sharp color tone, a high density and an excellent light-fastness and showing little indoor discoloration even when subjected to inkjet recording on ordinary paper and exhibits a good dyestuff solubility and a good dyestuff stability after prolonged storage, an aqueous inkjet recording liquid comprising the metal chelated dyestuff and an inkjet recording method using the aqueous inkjet recording liquid.

55 [0012] Another aim of the invention is to provide a metal chelated dyestuff for inkjet recording sufficiently excellent in properties such as saturation, print density, light-fastness, indoor discoloration resistance and storage stability even when it comprises copper incorporated therein as a metal element, an aqueous inkjet recording liquid comprising the metal chelated dyestuff and an inkjet recording method using the metal chelated dyestuff.

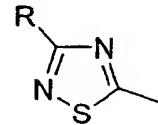
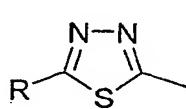
[0013] The metal chelated dyestuff for inkjet recording of the invention (Claim 1) is a water soluble azo metal chelated compound obtainable from an azo-based compound represented by the following general formula (1) having one or more hydrophilic groups per molecule and a metal element.

[0014] The metal chelated dyestuff for inkjet recording of the invention (Claim 2) is a water soluble azo metal chelated

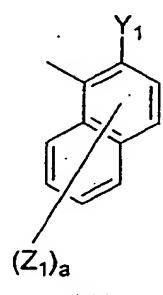
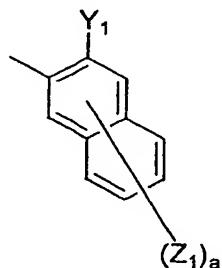
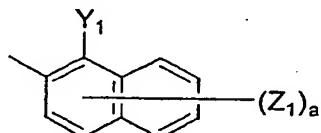
compound obtainable from an azo-based compound the free acid form of which is represented by the following general formula (1) and having one or more hydrophilic groups per molecule and a metal element,



10 wherein  $X_1$  represents a chain of a plurality of atoms containing a total of 2 or more hetero atoms of one or more kinds selected from the group consisting of nitrogen atom, oxygen atom and sulfur atom and wherein  $X_1$  is required to form at least one 5- to 7-membered heterocyclic ring; the heterocyclic ring containing  $X_1$  may have substituents thereon; 15 the substituents on the heterocyclic ring may further be condensed to form a condensed ring; the condensed heterocyclic ring containing  $X_1$  may be substituted, with the proviso that the heterocyclic ring containing  $X_1$  is not a heterocyclic ring represented by the following general formula (2) or (3); and  $Ar_1$  represents naphthyl group represented by any one of the following general formulae (4) to (6):



30 wherein R represents a hydrogen atom or an arbitrary substituent;



5 wherein  $Y_1$  represents a chelating group;  $Z_1$ 's represent arbitrary substituents which may be different from each other; and a represents an integer of from 0 to 6.

[0015] The aqueous inkjet recording liquid of the invention comprises an aqueous medium and one or more metal chelated dyestuffs for inkjet recording of the invention.

[0016] The inkjet recording method of the invention involves the use of such an aqueous inkjet recording liquid of the invention.

[0017] In other words, the inventors found that a water soluble dyestuff comprising a water soluble azo metal chelated compound of the aforementioned azo-based compound or a compound the free acid form of which is the aforementioned azo-based compound with a metal element can accomplish the aforementioned aim and thus worked out the invention.

[0018] The reason why the metal chelated compound of specific azo-based compound represented by the aforementioned general formula (1) is comprehensively excellent in print density, light-fastness, indoor discoloration resistance, storage stability, etc. as an inkjet recording dyestuff is unknown. However, it is presumed that the connection of the specific skeleton of the azo-based compound to diazo group causes the formation of a stable chelate with a metal

without deteriorating solubility, and thus providing a high saturation dyestuff.

[0019] Further, the metal chelated dyestuff of the invention is sufficiently excellent in saturation, print density, light-fastness, indoor discoloration resistance, storage stability, etc. even when it comprises copper, which is inexpensive and preferable in safety, incorporated therein as a metal element, and thus has an extremely high industrial value.

5 [0020] The invention will now be described in more detail below.

[0021] The metal chelated dyestuff for inkjet recording of the invention is a water soluble azo metal chelated compound obtainable from an azo-based compound represented by the general formula (1) having one or more hydrophilic groups per molecule or an azo-based compound the free acid form of which is represented by the general formula (1) and having one or more hydrophilic groups per molecule and a metal element,

10 [0022] In the general formula (1),  $X_1$  represents a chain of a plurality of atoms containing a total of 2 or more hetero atoms of one or more kinds selected from the group consisting of nitrogen atom, oxygen atom and sulfur atom and required to form at least one 5- to 7-membered heterocyclic ring. The heterocyclic ring containing  $X_1$  is preferably a heterocyclic ring having a nitrogen or oxygen atom at both ends of the carbon atom to which the azo group is connected to provide comprehensively excellent properties, including higher saturation, as an inkjet recording metal chelated dyestuff. Accordingly, in the atomic chain of  $X_1$ , the atom adjacent to the carbon atom to which the azo group is connected is preferably a nitrogen or oxygen atom. Particularly preferred examples of the heterocyclic ring containing  $X_1$  include triazole ring, tetrazole ring, oxadiazole ring, and thiadiazole ring. Preferred among these heterocyclic rings is triazole ring.

15 [0023] Unless mentioned otherwise, in the present invention the following definitions apply: an alkyl group which may be substituted is preferably an alkyl group having from 1 to 6 carbon atoms such as methyl and ethyl, carboxymethyl group, carboxyethyl group, trifluoromethyl group; an aryl group which may be substituted is preferably an aryl group having from 6 to 10 carbon atoms such as phenyl and naphthyl; an aralkyl group which may be substituted is preferably an aralkyl group having from 7 to 10 carbon atoms such as benzyl; an allyl which may be substituted is preferably an allyl group having from 3 to 9 carbon atoms such as vinyl and 2-propenyl; an alkoxy group which may be substituted is preferably an alkoxy group having from 1 to 6 carbon atoms such as methoxy and ethoxy; an aryloxy group which may be substituted is preferably an aryloxy group having 6 to 10 carbon atoms such as phenoxy; an acyloxy group which may be substituted is preferably an alkanoyloxy group having from 2 to 7 carbon atoms such as acetoxy, and benzoyloxy group, etc.; an alkoxycarbonyl group which may be substituted is preferably an alkoxycarbonyl group having from 2 to 7 carbon atoms such as methoxycarbonyl and ethoxycarbonyl; an aryloxycarbonyl group which may be substituted is preferably a phenoxy carbonyl group, naphthoxy carbonyl group, etc.;

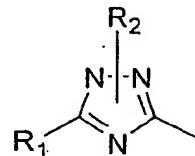
20 [0023] an acyl group which may be substituted is preferably an acyl group having from 2 to 10 carbon atoms such as acetyl; an amino group which may be substituted is preferably an alkylamino group having from 1 to 8 carbon atoms such as methylamino, ethylamino, dimethylamino and diethylamino; an acylamino group which may be substituted is preferably an alkanoylamino group having from 2 to 7 carbon atoms such as acetylamino, and benzoylamino group, etc.; a halogen atom is preferably chlorine, bromine, fluorine; an alkylthio group which may be substituted is preferably an alkylthio group having from 1 to 6 carbon atoms such as methylthio and ethylthio; an alkylsulfoxyl group which may be substituted is preferably an alkylsulfoxyl group having from 1 to 6 carbon atoms such as methylsulfoxyl and ethylsulfoxyl; and an alkylsulfonyl group which may be substituted is preferably an alkylsulfonyl group having from 1 to 6 carbon atoms such as methylsulfonyl and ethylsulfonyl.

25 [0024] The substituents mentioned in the above definitions are preferably selected from an alkyl group, alkoxy group, halogenated alkyl group (preferably perhalogenated alkyl group, more preferably perfluorinated alkyl group) (wherein the alkyl group or alkoxy group preferably has not greater than 10 carbon atoms, more preferably not greater than 6 carbon atoms, particularly from not smaller than 1 to not greater than 5 carbon atoms), carboxyl group, hydroxy group and cyano group. Preferred among these substituents are alkyl group, perfluoroalkyl group, carboxyl group, hydroxy group and cyano group. Particularly preferred among these substituents are carboxyl group and cyano group because they can easily provide a metal chelated dyestuff for inkjet recording with higher saturation.

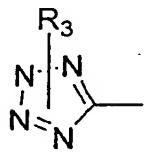
30 [0025] The heterocyclic ring containing  $X_1$  may have one or more substituents thereon. The substituents on the heterocyclic ring may be further condensed to form a condensed ring. (e.g. a condensed 5- to 7-membered ring). In this case, the substituents on the heterocyclic or condensed ring each independently are one selected from the group consisting of alkyl group which may be substituted (e.g., alkyl group having from 1 to 6 carbon atoms such as methyl and ethyl, carboxymethyl group, carboxyethyl group, trifluoromethyl group), aryl group which may be substituted (preferably aryl group having from 6 to 10 carbon atoms such as phenyl and naphthyl), aralkyl group which may be substituted (preferably aralkyl group having from 7 to 10 carbon atoms such as benzyl), allyl group which may be substituted (preferably allyl group having from 3 to 9 carbon atoms such as vinyl and 2-propenyl), alkoxy group which may be substituted (preferably alkoxy group having from 1 to 6 carbon atoms such as methoxy and ethoxy), aryloxy group which may be substituted (e.g. preferably aryloxy group having 6 to 10 carbon atoms such as phenoxy), acyloxy group which may be substituted (preferably alkanoyloxy group having from 2 to 7 carbon atoms such as acetoxy, and benzoyloxy group, etc.), alkoxycarbonyl group which may be substituted (preferably alkoxycarbonyl group having from

2 to 7 carbon atoms such as methoxycarbonyl and ethoxycarbonyl), aryloxycarbonyl group which may be substituted (preferably phenoxy carbonyl group, naphthoxy carbonyl group, etc.), carbamoyl group which may be substituted, acyl group which may be substituted (preferably acyl group having from 2 to 10 carbon atoms such as acetyl), carboxyl group, hydroxyl group, cyano group, amino group which may be substituted (e.g., alkylamino group having from 1 to 8 carbon atoms such as methylamino, ethylamino, dimethylamino and diethylamino), acylamino group which may be substituted (e.g. alkanoylamino group having from 2 to 7 carbon atoms such as acetylamino, and benzoylamino group, etc.), nitro group, halogen atom (e.g., chlorine, bromine, fluorine), phosphono group, sulfo group, mercapto group, alkylthio group which may be substituted (e.g. alkylthio group having from 1 to 6 carbon atoms such as methylthio and ethylthio), alkylsulfonyl group which may be substituted (e.g. alkylsulfonyl group having from 1 to 6 carbon atoms such as methylsulfonyl and ethylsulfonyl) and thiocyanato group.

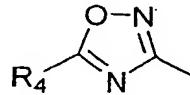
[0026] In particular, the heterocyclic ring containing  $X_1$  is preferably one represented by any one of the following general formulae (7) to (11).



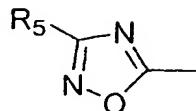
wherein  $R_1$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, carbamoyl group, hydroxyl group, acyl group which may be substituted, cyano group, amino group which may be substituted, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, mercapto group, alkylthio group which may be substituted, alkylsulfonyl group which may be substituted or thiocyanato group;  $R_2$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted or allyl group which may be substituted; and  $R_1$  and  $R_2$  may form a condensed ring together with a triazole ring.



wherein  $R_3$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, carbamoyl group, hydroxyl group, cyano group or sulfo group.



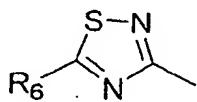
wherein  $R_4$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group which may be substituted.



(10)

10 wherein R<sub>5</sub> represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group which may be substituted.

15



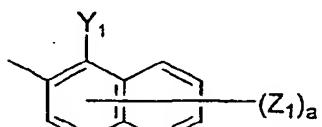
(11)

25 wherein R<sub>6</sub> represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group which may be substituted.

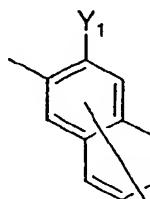
30 [0027] In the case where R<sub>1</sub> to R<sub>6</sub> in the general formulae (7) to (11) have substituents, examples of the substituents include alkyl or alkoxy group having not greater than 10 carbon atoms, preferably not greater than 6 carbon atoms, particularly from not smaller than 1 to not greater than 5 carbon atoms, carboxyl group, and cyano group. Preferred among these substituents are alkyl group, carboxyl group, and cyano group. Particularly preferred among these substituents are carboxyl group and cyano group because they can easily provide a metal chelated dyestuff for inkjet recording with higher saturation.

35 [0028] Preferred among the heterocyclic rings represented by the general formulae (7) to (11) is the triazole ring represented by the general formula (7) because it can provide a metal chelated dyestuff with higher saturation.

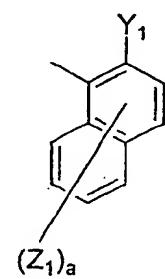
[0029] Ar<sub>1</sub> in the general formula (1) is a naphthyl group represented by any one of the following general formulae (4) to (6).



(4)



(5)



(6)

55 [0030] In the general formulae (4) to (6), Y<sub>1</sub> represents a chelating group, preferably hydroxyl group, carboxyl group, amino group which may be substituted (e.g., amino group, methylamino group, bis(2-hydroxyethyl)amino group), sulfo group, carbamoyl group, alkoxy group which may be substituted (preferably alkoxy group having from 1 to 6 carbon atoms such as methoxy, carbonyl and 2-hydroxyethoxy group), alkylthio group which may be substituted (preferably alkylthio group having from 1 to 6 carbon atoms such as methylthio and 2-hydroxyethylthio), alkylsulfonylamino group which may be substituted (preferably alkylsulfonylamino group having from 1 to 6 carbon atoms such as methylsulfo-

nylamino) or arylsulfonylamino group which may be substituted (e.g., benzenesulfonylamino group). Preferred among the groups of  $Y_1$  is hydroxyl group.

[0031] In the general formulae (4) to (6), the  $Z_1$ 's each independently are preferably selected from the group consisting of alkoxy group which may be substituted (e.g. alkoxy group having from 1 to 6 carbon atoms such as methoxy and ethoxy), aryloxy group which may be substituted (preferably an aryloxy group having 6 to 10 carbon atoms, e.g. phenoxy group) acyloxy group which may be substituted (e.g. alkanoyloxy group having from 2 to 7 carbon atoms such as acetoxy, and benzyloxy group, etc.), alkoxy carbonyl group which may be substituted (e.g. alkoxy carbonyl group having from 2 to 7 carbon atoms such as methoxycarbonyl and ethoxycarbonyl), aryloxy carbonyl group which may be substituted (preferably having 6 to 10 carbon atoms in the aryl moiety, e.g. phenoxy carbonyl group, naphthoxy carbonyl group), carboxyl group, carbamoyl group which may be substituted (e.g., carbamoyl group), carboxyanilide group which may be substituted (e.g., 3-sulfocarboxyanilide group), hydroxyl group, amino group which may be substituted (e.g. alkylamino group having from 1 to 6 carbon atoms such as amino and methylamino), ureide group, acylamino group which may be substituted (e.g. alkanoylamino group having from 2 to 7 carbon atoms such as acetylamino, and benzoylamino group, etc.), alkylsulfonylamino group which may be substituted (e.g. alkylsulfonylamino group having from 1 to 6 carbon atoms such as methylsulfonylamino), arylsulfonylamino group which may be substituted (e.g., phenylsulfonylamino group, 4-methylphenylsulfonyl-amino group), phosphono group, sulfo group and sulfamoyl group which may be substituted (e.g., sulfamoyl group, N,N-bis(carboxymethyl)sulfamoyl group). The suffix a represents an integer of from 0 to 6.

[0032]  $Z_1$ , if the carbon connected to the azo group is at the 1-position, is preferably connected to the carbon at the 3-position because it can easily provide a metal chelated dyestuff with higher saturation.  $Z_1$  is also preferably a carboxyl group, carbamoyl group which may be substituted, sulfo group or sulfamoyl group which may be substituted. Preferred among these groups are sulfo group and sulfamoyl group which may be substituted because they can easily provide a metal chelated dyestuff with higher saturation.

[0033] Particularly preferred among the naphthyl groups  $Ar_1$  represented by the general formulae (4) to (6) is  $\alpha$ -naphthyl group represented by the general formula (6) because it can easily provide a metal chelated dyestuff with higher saturation.

[0034] The azo-based compound represented by the general formula (1) is a compound having at least one hydrophilic group per molecule. Examples of such a hydrophilic group include sulfo group, carboxyl group, hydroxyl group, amino group, and phosphono group. Preferred among these hydrophilic groups are sulfo group and carboxyl group.

[0035] In the invention, examples of the metal element usually in the form of the metal compound such as a salt, which forms a chelated compound with the azo-based compound represented by the general formula (1) include silver (I), aluminum (III), gold (III), cerium (III, IV), cobalt (II, III), chromium (III), copper (I, II), europium (III), iron (II, III), gallium (III), germanium (IV), indium (III), lanthanum (III), manganese (II), nickel (II), palladium (II), platinum (II, IV), rhodium (II, III), ruthenium (II, III, IV), scandium (III), silicon (IV), samarium (III), titanium (IV), uranium (IV), zinc (II), and zirconium (IV). Preferred among these metals are nickel (II), cobalt (II, III), copper (II), iron (II, III), and zinc (II). From the standpoint of price and environmental protection, copper (II) is more desirable.

[0036] Examples of the anion of metal salt to be used in the production of the chelated compound include monovalent or divalent anions such as  $Cl^-$ ,  $Br^-$ ,  $CH_3COO^-$  and  $SO_4^{2-}$ .

[0037] In the case where the hydrophilic group in the azo-based compound represented by the general formula (1) is an acid group as mentioned above, the metal chelated dyestuff of the invention may be used with its acid group kept in the form of free acid. In the case where the hydrophilic group in the azo-based compound has been produced in the form of salt, the metal chelated dyestuff of the invention may be used as it is or may be converted to a desired salt form before use. The acid group may be partly in the form of a salt. A salt type dyestuff and a free acid type dyestuff may be present in admixture. Examples of such a salt includes the salts of alkaline metal such as Na, Li and K, ammonium salts which may be substituted by alkyl group or hydroxyalkyl group, and organic amine salts. Examples of the organic amine include lower alkylamine, hydroxy-substituted lower alkylamine, carboxy-substituted lower alkylamine, and polyamine having from 2 to 10 alkyleneimine units having from 2 to 4 carbon atoms (lower alkyl is e.g. an alkyl having 1 to 6 carbon atoms). The number of the kinds of salt to be used is not limited to one. A plurality of salts may be present in admixture.

[0038] In the structure of the metal chelated dyestuff of the invention, if a plurality of acid groups are incorporated in its molecule, they may be in the form of either salt or acid or may be different from each other.

[0039] Specific examples of the metal chelated dyestuff of the invention include chelated dyestuffs of azo-based compounds formed by heterocyclic rings containing  $X_1$  set forth in Tables 1 to 6 and  $Ar_1$  set forth in Tables 7 and 8 in arbitrary combination with metal elements e.g., nickel acetate or copper acetate, but the invention is not limited thereto.

Table 1

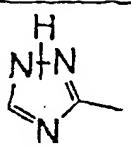
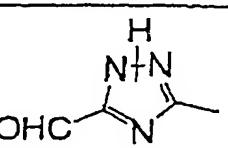
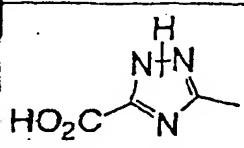
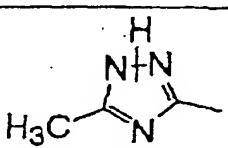
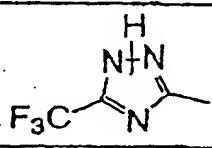
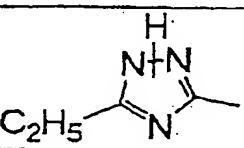
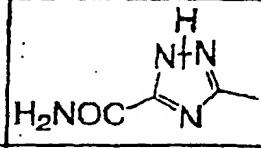
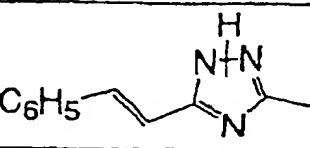
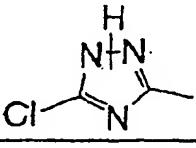
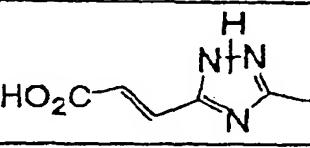
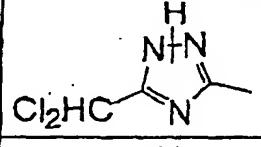
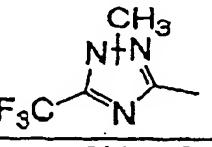
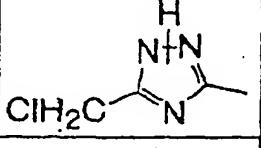
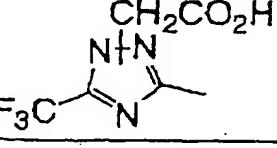
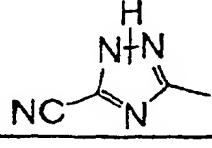
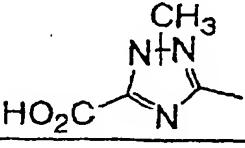
No.			
1-1		1-9	
1-2		1-10	
1-3		1-11	
1-4		1-12	
1-5		1-13	
1-6		1-14	
1-7		1-15	
1-8		1-16	

Table 2

No.			
1-17		1-20	
1-18		1-21	
1-19		1-22	

Table 3

No.			
2-1		2-5	
2-2		2-6	
2-3		2-7	
2-4			

Table 4

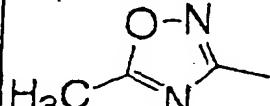
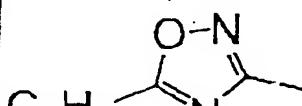
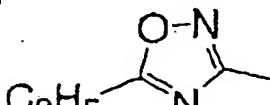
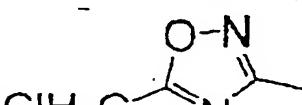
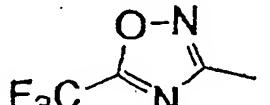
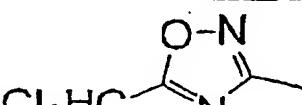
No.			
3-1		3-4	
3-2		3-5	
3-3		3-6	

Table 5

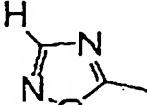
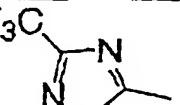
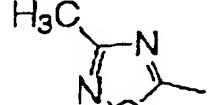
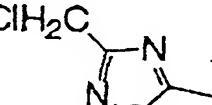
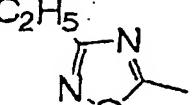
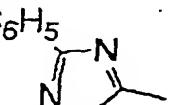
No.			
4-1		4-4	
4-2		4-5	
4-3		4-6	

Table 6

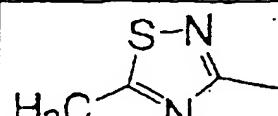
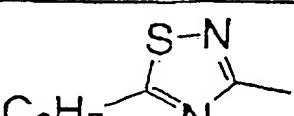
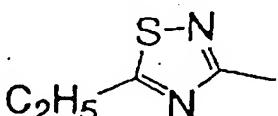
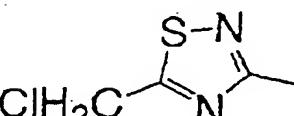
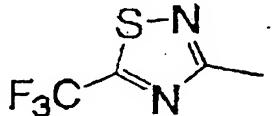
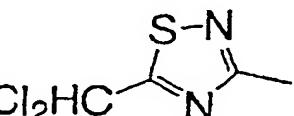
No.			
5-1		5-4	
5-2		5-5	
5-3		5-6	

Table 7

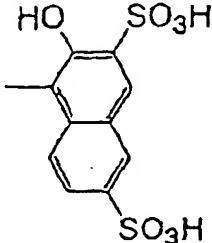
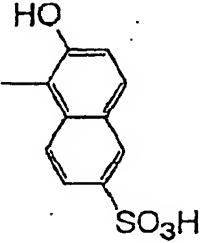
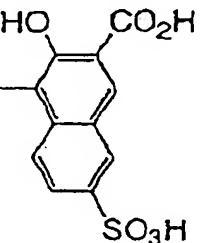
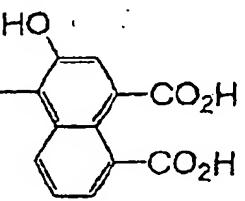
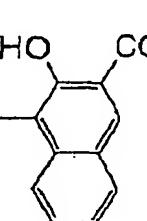
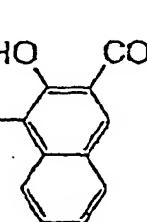
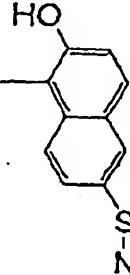
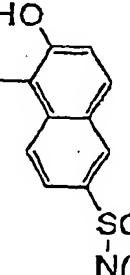
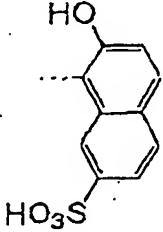
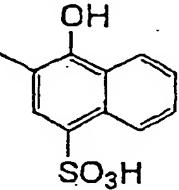
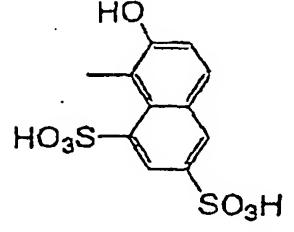
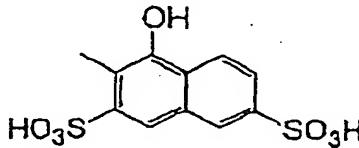
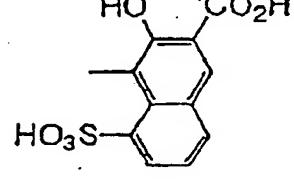
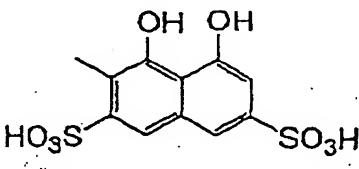
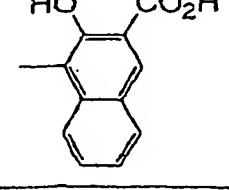
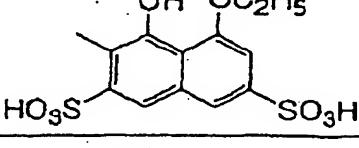
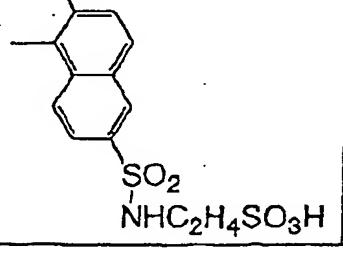
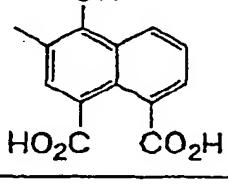
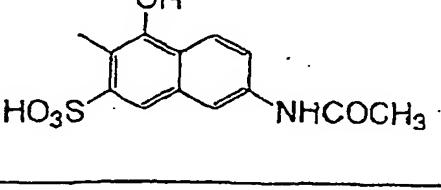
No.	Ar <sub>1</sub>
6-1	
6-2	
6-3	
6-4	
6-5	
6-6	
6-7	
6-8	

Table 8

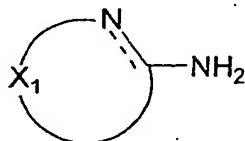
No.	Ar <sub>1</sub>
6-9	
6-14	
6-10	
6-15	
6-11	
6-16	
6-12	
6-17	
6-13	
6-18	
6-19	

[0040] The azo metal chelated compound according to the invention can be produced from an azo-based compound represented by the general formula (1) or an azo-based compound the free acid form of which is represented by the general formula (1) and a metal compound.

[0041] The azo-based compound represented by the general formula (1) can be produced by any known method,

e.g., by subjecting a heteroamine compound represented by the following general formula (in which  $X_1$  is as defined in the general formula (1)) to diazotization according to diazotization coupling method to cause coupling with  $H-Ar_1$  (in which  $Ar_1$  is as defined in the general formula (1)).

5



10

[0042] The azo-based compound thus obtained can be then reacted with a metal compound (e.g., NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O) to produce a water soluble azo metal chelated compound according to the invention.

[0043] In the water soluble azo metal chelated compound according to the invention, the number of azo-based compounds represented by the general formula (1) to be coordinated to the metal element as ligands varies with the azo-based compound and metal compound used. In practice, however, the number of azo-based compounds represented by the general formula (1) to be coordinated is from 1 to 2 per metal element. The molecular weight of the water soluble azo metal chelated compound is preferably not greater than 2,000, particularly from 500 to 1,500 as calculated in terms of molecular weight excluding that of metal element, taking into account the solubility and storage stability for use in inkjet recording.

[0044] The aqueous inkjet recording liquid of the invention comprises an aqueous medium and one or more metal chelated dyestuffs for inkjet recording of the invention.

[0045] The content of the aforementioned metal chelated dyestuff in the aqueous inkjet recording liquid of the invention is preferably from 0.5% to 10% by weight, particularly from 2% to 5% by weight based on the total weight of the recording liquid as calculated in terms of water soluble azo metal chelated compound if the aqueous inkjet recording liquid is used as a dark color ink or preferably from 0.1% to 2% by weight, particularly from 0.1% to 1.5% by weight based on the total weight of the recording liquid as calculated in terms of water soluble azo metal chelated compound if the aqueous inkjet recording liquid is used as a light color ink.

[0046] As the aqueous medium to be used in the recording liquid of the invention there is preferably used a mixture of water and a water soluble organic solvent. Examples of the water soluble organic solvent to be mixed with water include ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol (weight-average molecular weight: approx. 190 to 400), glycerin, N-methylpyrrolidone, N-ethylpyrrolidone, 1,3-dimethylimidazolidinone, thiodiethanol, dimethyl sulfoxide, ethylene glycol monoallyl ether, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, 2-pyrrolidone, sulfolane, ethyl alcohol, and isopropanol. Such a water soluble organic solvent is normally used in an amount of from 1% to 45% by weight based on the total weight of the recording liquid. On the other hand, water is used in an amount of from 50% to 95% by weight based on the total weight of the recording liquid.

[0047] The recording liquid of the invention may comprise dyestuffs other than the metal chelated dyestuff of the invention and other additives incorporated therein.

[0048] The recording liquid of the invention may comprise a compound selected from the group consisting of urea, thiourea, biuret and semicarbazide incorporated therein in an amount of from about 0.1 to 10% by weight, preferably from about 0.5% to 5% by weight based on the total weight thereof or a surface active agent incorporated therein in an amount of from about 0.001% to 5% by weight based on the total weight thereof to further improve the quick-drying properties after printing and the print quality.

[0049] The pH value of the recording liquid of the invention is normally not lower than 4, preferably not lower than 6, more preferably not lower than 6.5, most preferably not lower than 7. The upper limit of the pH value of the recording liquid of the invention is normally not higher than 11, preferably not higher than 10, more preferably not higher than 9.5. In particular, the recording liquid is preferably within the range of from neutral to slightly alkaline to form a metal chelate of azo-based compound in a stable manner.

[0050] When the pH value of the recording liquid is too low beyond this range, i.e., falls below 4, the azo metal chelated compound of dyestuff exhibits an inferior dissolution stability to cause the precipitation of dyestuff during storage or dislocation of the metal chelate that can lead to discoloration. When the pH value of the recording liquid exceeds 11, the alcohol-based organic solvent and the metal chelate together form an alcholate in the recording liquid, possibly causing the deterioration of the ink properties. Further, the recording liquid of the invention can be brought into contact with the human body and thus is preferably prepared such that it is not provided with a high pH value from the standpoint of safety.

[0051] The pH value of the recording liquid can be adjusted with a pH adjustor. In this case, as the pH adjustor there

may be used any material so far as it can control the pH value of the recording liquid to a desired range without having any adverse effects on the recording- liquid to be prepared. Specific examples of the pH adjustor which is preferably used herein include hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and ammonium hydroxide, inorganic acid salts of alkaline metals such as sodium carbonate, sodium hydrogencarbonate, potassium carbonate, lithium carbonate, sodium phosphate, potassium phosphate, lithium phosphate, potassium dihydrogenphosphate and disodium hydrogenphosphate, organic acid salts of alkaline metals such as sodium acetate, potassium acetate, lithium acetate, sodium oxalate, potassium oxalate, lithium oxalate, sodium borate, sodium tetraborate, potassium hydrogenphthalate and potassium hydrogentartrate, ammonia, amines such as methylamine, ethylamine, diethylamine, tris(hydroxymethyl)aminomethane hydrochloride, diethanolamine, triethanolamine, morpholine and propanolamine, 4-morpholine ethanesulfonate, and 4-morpholine propanesulfonate.

[0052] Preferred among these pH adjustors is a buffer having a buffering action. Examples of the buffer include a combination (mixture) of weak acid and salt thereof, or a combination (mixture) of weak base and salt thereof. Specific examples of the buffer include sodium acetate, lithium acetate, sodium phosphate, lithium phosphate, potassium dihydrogenphosphate, disodium hydrogenphosphate, sodium borate, sodium tetraborate, tris(hydroxymethyl) aminomethane hydrochloride, 4-morpholine ethanesulfonate, and 4-morpholine propanesulfonate. Preferred among these buffers are tris(hydroxymethyl) aminomethane hydrochloride, 4-morpholine ethanesulfonate, and 4-morpholine propanesulfonate.

[0053] The buffer is normally used in an amount of from 0.01% to 3% by weight, preferably from 0.1% to 1% by weight, more preferably from 0.1% to 0.5% by weight based on the total weight of the recording liquid.

[0054] Alternatively, the pH value of the recording liquid may be adjusted with a buffering solution. As such a buffering solution there may be normally used any buffering solution which is widely used for the purpose of inhibiting the drop of pH value caused by the incorporation of hydrogen ion, for example, systems comprising various materials incorporated therein in a proper amount in the form of the following combinations, etc. A proper buffering solution may be selected from these buffering solutions.

A combination of potassium hydrogenphthalate and sodium hydroxide,  
 a combination of potassium dihydrogenphosphate and sodium hydroxide,  
 a combination of boric acid, potassium chloride and sodium hydroxide,  
 a combination of glycine, sodium chloride and hydrochloric acid,  
 a combination of glycine, sodium chloride and sodium hydroxide,  
 a combination of sodium citrate and hydrochloric acid, a combination of sodium citrate and sodium hydroxide,  
 a combination of sodium tetraborate (borax) and hydrochloric acid,  
 a combination of sodium tetraborate (borax) and sodium hydroxide,  
 a combination of potassium dihydrogenphosphate and disodium hydrogenphosphate,  
 a combination of potassium dihydrogencitrate and sodium hydroxide,  
 a combination of succinic acid and sodium tetraborate,  
 a combination of potassium dihydrogencitrate and sodium tetraborate,  
 a combination of potassium dihydrogenphosphate and sodium tetraborate,  
 a combination of sodium tetraborate and sodium carbonate,  
 a combination of hydrochloric acid and sodium carbonate,  
 a combination of tartaric acid and sodium tartrate,  
 a combination of lactic acid and sodium lactate,  
 a combination of acetic acid and sodium acetate,  
 a combination of ammonium chloride and ammonia,  
 a combination of sodium diethylbarbiturate, sodium acetate and hydrochloric acid,  
 a combination of sodium diethylbarbiturate and hydrochloric acid,  
 a combination of N,N-diethylglycine sodium salt and hydrochloric acid,  
 a combination of disodium hydrogenphosphate and citric acid,  
 a combination of citric acid, potassium dihydrogenphosphate, boric acid, diethylbarbituric acid and trisodium phosphate,  
 a combination of boric acid, citric acid and trisodium phosphate,  
 a combination of 2,4,6-trimethylpyridine and hydrochloric acid,  
 a combination of tris(hydroxymethyl)aminomethane and hydrochloric acid,  
 a combination of 2-amino-2-methyl-1,3-propanediol and hydrochloric acid,  
 a combination of 3-[4-(2-hydroxyethyl)-1-piperadiny]-1-propanesulfonic acid, sodium hydroxide and sodium chloride,  
 and  
 a combination of citric acid, potassium dihydrogenphosphate, sodium tetraborate, tris(hydroxymethyl)aminomethane, potassium chloride and sodium hydroxide

[0055] Preferred among these buffering solutions are as follows.

A combination of potassium dihydrogenphosphate and sodium hydroxide,

a combination of boric acid, potassium chloride and sodium hydroxide,  
 a combination of sodium tetraborate (borax) and hydrochloric acid,  
 a combination of sodium tetraborate (borax) and sodium hydroxide,  
 a combination of potassium dihydrogenphosphate and disodium hydrogenphosphate,  
 5 a combination of potassium dihydrogenphosphate and sodium tetraborate,  
 a combination of ammonium chloride and ammonia, and  
 a combination of tris(hydroxymethyl)aminomethane and hydrochloric acid

[0056] Particularly preferred among these buffers are as follows.

A combination of sodium tetraborate (borax) and sodium hydroxide and  
 10 a combination of tris(hydroxymethyl)aminomethane and hydrochloric acid

[0057] The buffering solution is normally used in an amount of from 0.1% to 40% by weight, preferably from 0.5% to 30% by weight, more preferably from 1% to 25% by weight based on the total weight of the recording liquid.

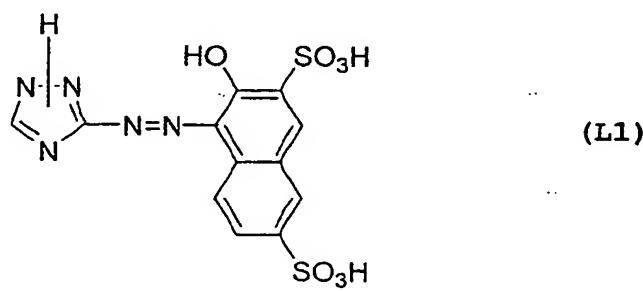
[0058] In accordance with the inkjet recording method of the invention, droplets of such an aqueous inkjet recording liquid of the invention are ejected by an ordinary method to effect printing, making it possible to obtain a high quality printed matter.

[0059] The invention will be further described in the following synthesis examples and examples, but the invention is not limited thereto so far as it does not deviate from the scope of the claims.

Synthesis Example 1: Synthesis of azo-based compound by diazotization coupling process

[0060] A solution obtained by adding 10.0 g of 3-amino-1,2,4-triazole to 82.7 g of a 40% sulfuric acid was cooled to a temperature of from 0°C to 5°C where 20.8 g of a 38% aqueous solution of sodium nitrite was then added thereto to cause diazotization.

[0061] Subsequently, to the solution was added sulfamic acid so that excess sodium sulfite was decomposed to obtain a diazo solution. Separately, 35.0 g of disodium 2-naphthol-3,6-disulfonate was dissolved in 400 ml of water. To the solution was then added 2.3 g of sulfamic acid. To the solution was then added dropwise the diazo solution previously mentioned at a temperature of from 0°C to 5°C while the pH value thereof was being adjusted with an aqueous solution of NaOH to a range of from 8.0 to 9.0. To the resulting slurry was then added 25 g of sodium chloride. The resulting solid content was withdrawn by filtration, and then washed with an aqueous solution of sodium chloride. The resulting solid content was then dissolved in 400 ml of water under heating to a temperature of 60°C. The solution was then allowed to cool to room temperature. To the solution was then added 400 ml of isopropanol. The resulting solid content was withdrawn by filtration, washed, and then dried to obtain 39.2 g of an azo dyestuff represented by the following structural formula (L1).



50 Synthesis Example 2: Synthesis of nickel chelated dyestuff

[0062] To 5.0 g of the azo dyestuff of the structural formula (L1) synthesized in Synthesis Example 1 was added 200 ml of water. The mixture was then adjusted to pH 10.0 with an aqueous solution of NaOH to make a solution. To the solution was then added dropwise a solution of 1.3 g of nickel acetate (II) tetrahydrate in 26 ml of water at a temperature of from 15°C to 25°C. During the reaction, the pH value of the reaction solution was adjusted to a range of from 9.0 to 10.0. The dyestuff solution thus obtained was then desalinated by a table electrodialysis device (Microacylizer S3, produced by Asahi Kasei Corp.). The residual aqueous solution was then concentrated. To the aqueous solution of dyestuff was then added isopropyl alcohol to produce a precipitate which was withdrawn by filtration, and then dried to obtain

3.5 g of a nickel chelated dyestuff.

[0063] The nickel chelated dyestuff (D-1) thus obtained exhibited a maximum absorption wavelength of 522 nm (in water).

5 Synthesis Example 3: Synthesis of copper chelated dyestuff

[0064] To 5.0 g of the azo dyestuff of the structural formula (L1) synthesized in Synthesis Example 1 was added 200 ml of water. The mixture was then adjusted to pH 10.0 with an aqueous solution of NaOH to make a solution. To the solution was then added dropwise a solution of 2.1 g of copper acetate (II) monohydrate in 42 ml of water at a temperature of from 15°C to 25°C. During the reaction, the pH value of the reaction solution was adjusted to a range of from 9.0 to 10.0. The dyestuff solution thus obtained was then desalinated by a table electrodialysis device (Microacylizer S3, produced by Asahi Kasei Corp.). The residual aqueous solution was then concentrated. To the aqueous solution of dyestuff was then added isopropyl alcohol to produce a precipitate which was withdrawn by filtration, and then dried to obtain 3.5 g of a copper chelated dyestuff.

[0065] The copper chelated dyestuff (D-2) thus obtained exhibited a maximum absorption wavelength of 535 nm (in water).

Synthesis Example 4: Synthesis of nickel chelated dyestuff

[0066] A dyestuff (L2) comprising No. 1-2 of Table 1 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L2) thus obtained was then processed in the same manner as in Synthesis Example 2 to synthesize a nickel chelated dyestuff comprising the azo dyestuff (L2) and nickel acetate.

[0067] The nickel chelated dyestuff (D-3) thus obtained exhibited a maximum absorption wavelength of 533 nm (in water).

5 Synthesis Example 5: Synthesis of copper chelated dyestuff

[0068] A dyestuff (L2) comprising No. 1-2 of Table 1 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L2) thus obtained was then processed in the same manner as in Synthesis Example 3 to synthesize a copper chelated dyestuff comprising the azo dyestuff (L2) and copper acetate.

[0069] The copper chelated dyestuff (D-4) thus obtained exhibited a maximum absorption wavelength of 540 nm (in water).

5 Synthesis Example 6: Synthesis of nickel chelated dyestuff

[0070] A dyestuff (L3) comprising No. 1-18 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L3) thus obtained was then processed in the same manner as in Synthesis Example 2 to synthesize a nickel chelated dyestuff comprising the azo dyestuff (L3) and nickel acetate.

[0071] The nickel chelated dyestuff (D-5) thus obtained exhibited a maximum absorption wavelength of 515 nm (in water).

Synthesis Example 7: Synthesis of copper chelated dyestuff

[0072] A dyestuff (L3) comprising No. 1-18 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L3) thus obtained was then processed in the same manner as in Synthesis Example 3 to synthesize a copper chelated dyestuff comprising the azo dyestuff (L3) and copper acetate.

[0073] The copper chelated dyestuff (D-6) thus obtained exhibited a maximum absorption wavelength of 548 nm (in water).

Synthesis Example 8: Synthesis of nickel chelated dyestuff

[0074] A dyestuff (L4) comprising No. 1-17 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L4) thus obtained was then processed in the same manner as in Synthesis Example 2 to synthesize a nickel chelated dyestuff comprising the azo dyestuff (L4) and nickel acetate.

[0075] The nickel chelated dyestuff (D-7) thus obtained exhibited a maximum absorption wavelength of 516 nm (in water).

EP 1 270 676 A1

Synthesis Example 9: Synthesis of copper chelated dyestuff

[0076] A dyestuff (L4) comprising No. 1-17 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L4) thus obtained was then processed in the same manner as in Synthesis Example 3 to synthesize a copper chelated dyestuff comprising the azo dyestuff (L4) and copper acetate.

[0077] The copper chelated dyestuff (D-8) thus obtained exhibited a maximum absorption wavelength of 554 nm (in water).

10 Synthesis Example 10: Synthesis of nickel chelated dyestuff

[0078] A dyestuff (L5) comprising No. 1-19 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L5) thus obtained was then processed in the same manner as in Synthesis Example 2 to synthesize a nickel chelated dyestuff comprising the azo dyestuff (L5) and nickel acetate.

[0079] The nickel chelated dyestuff (D-9) thus obtained exhibited a maximum absorption wavelength of 535 nm (in water).

Synthesis Example 11: Synthesis of copper chelated dyestuff

20 [0080] A dyestuff (L5) comprising No. 1-19 of Table 2 and No. 6-1 of Table 7 in combination was synthesized in the same manner as in Synthesis Example 1. The azo dyestuff (L5) thus obtained was then processed in the same manner as in Synthesis Example 3 to synthesize a copper chelated dyestuff comprising the azo dyestuff (L5) and copper acetate.

25 [0081] The copper chelated dyestuff (D-10) thus obtained exhibited a maximum absorption wavelength of 543 nm (in water).

EXAMPLE 1

30 [0082] To 10 parts by weight of diethylene glycol, 3 parts by weight of diethylene glycol monobutyl ether and 3.0 parts by weight of the nickel chelated dyestuff (D-1) obtained in Synthesis Example 2 was added water. The aqueous solution was then adjusted with an aqueous solution of sodium hydroxide to pH 9 to make 100 parts by weight. The composition was then thoroughly stirred for dissolution. The solution was filtered through a teflon (trade name) filter having a pore diameter of 1  $\mu$ m under pressure, and then subjected to deaeration by a vacuum pump and an ultrasonic cleaner to prepare a recording liquid.

35 [0083] Using an inkjet printer (trade name "PM-750C", produced by SEIKO EPSON CORPORATION), the recording liquid thus obtained was subjected to inkjet recording on an electrophotographic paper (trade name "4024 paper", produced by Xerox Corp.), a superfine dedicated paper (trade name "MJA4SP1", produced by SEIKO EPSON CORPORATION), a superfine dedicated glossy paper (trade name "MJA4SP3", produced by SEIKO EPSON CORPORATION) and a dedicated photoprint paper (trade name "PMA4SP1", produced by SEIKO EPSON CORPORATION). As a result, a sharp bluish magenta-colored printed matter.

40 [0084] The printed matter and the recording liquid thus obtained were then subjected to the following tests. The results are set forth in Table 9.

45 Light-fastness test

[0085] Using a xenon fadeometer (produced by Atlas Co., Ltd.), the printed matter was irradiated with light for 80 hours, and then observed for discoloration.

50 Indoor discoloration test

[0086] The printed matter was observed for discoloration after 2 hours of storage in an optically-shielded tank having an ozone concentration of 3 ppm.

55 Print quality test

[0087] The printed matter was measured for saturation by means of Gretag Macbeth SPM50 (produced by Gretag Macbeth Corp.). All the printed matters were confirmed to have a high saturation.

Test on storage stability of recording liquid

[0088] The recording liquid was examined for change after 1 month of storage at a temperature of 5°C and 60°C in a sealed polytetrafluoroethylene container.

EXAMPLES 2 TO 6

[0089] Recording liquids were prepared in the same manner as in Example 1 except that as dyestuffs there were used chelated dyestuffs set forth in Table 9, respectively. The recording liquids thus prepared were each subjected to printing in the same manner as in Example 1. All the recording liquids provided a sharp magenta-colored printed matter.

[0090] The printed matters and the recording liquids thus obtained were then subjected to various tests in the same manner as in Example 1. The results are set forth in Table 9.

COMPARATIVE EXAMPLE 1

[0091] A recording liquid was prepared in the same manner as in Example 1 except that the nickel chelated dyestuff (D-1) obtained in Synthesis Example 2 was replaced by the dyestuff of Example 1 in Japanese Patent Application No. 2000-390195 (corresponding to Japanese Patent Laid-Open No. 2002-80765). The recording liquid thus prepared was subjected to printing in the same manner as in Example 1. As a result, the recording liquid provided a sharp magenta-colored printed matter.

[0092] The printed matter and the recording liquid thus obtained were then subjected to various tests in the same manner as in Example 1. The results are set forth in Table 9.

COMPARATIVE EXAMPLE 2

[0093] A recording liquid was prepared in the same manner as in Example 1 except that the nickel chelated dyestuff (D-1) obtained in Synthesis Example 2 was replaced by the dyestuff of Example 2 in Japanese Patent Application No. 2000-390195 (corresponding to Japanese Patent Laid-Open No. 2002-80765). The recording liquid thus prepared was subjected to printing in the same manner as in Example 1. As a result, the recording liquid provided a sharp magenta-colored printed matter.

[0094] The printed matter and the recording liquid thus obtained were then subjected to various tests in the same manner as in Example 1. The results are set forth in Table 9.

Table 9

	Example Nos.						Comparative Example Nos.
	1	2	3	4	5	6	
Chelated dyestuff of recording liquid	Nickel chelated dyestuff (D-1)	Copper chelated dyestuff (D-2)	Nickel chelated dyestuff (D-3)	Copper chelated dyestuff (D-4)	Nickel chelated dyestuff (D-5)	Copper chelated dyestuff (D-6)	Dyestuff of Example 1 in Japanese Patent Application No. 2000-390195
	Electro-photogra- phic paper	Small discolora- tion	Dyestuff of Example 2 in Japanese Patent Application No. 2000-390195				
Light- fastness test	Superfine dedicated paper	Small discolora- tion					
	Superfine dedicated glossy paper	Small discolora- tion					
	Dedicated Photoprint Paper	Small discolora- tion					

Table 9 (cont'd)

		Example Nos.						Comparative Example Nos.	
		1	2	3	4	5	6	1	2
Indoor discolora- tion test	Electro- photogra- phic Paper	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion
	Superfine dedicated Paper	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Great discolora- tion	Great discolora- tion
	Superfine dedicated glossy Paper	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Medium discolora- tion	Medium discolora- tion
	Dedicated Photoprint Paper	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Small discolora- tion	Great discolora- tion	Great discolora- tion
	Test on storage stability of recording liquid		No precipita- tion of insoluble matters at any temper- ature, good storage stability						

[0095] The metal chelated dyestuff for inkjet recording of the invention exhibits excellent water solubility. The recording liquid of the invention comprising the metal chelated dyestuff can provide a sharp recorded matter when printed on ordinary paper and dedicated paper as an aqueous inkjet recording liquid. The recorded matter exhibits excellent print density, light-fastness and indoor discoloration resistance. The recording liquid of the invention exhibits good storage stability.

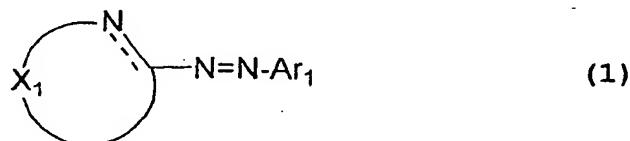
[0096] In accordance with the inkjet recording method of the invention, the use of the recording liquid of the invention makes it possible to obtain a high quality printed matter.

[0097] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0098] This application is based on Japanese patent applications No. 2001-185245 filed on June 19, 2001, and No. 2002-165893 filed on June 6, 2002, the entire contents thereof being hereby incorporated by reference.

15 Claims

1. A metal chelated dyestuff for inkjet recording which is a water-soluble azo metal chelated compound obtainable from an azo-based compound represented by the following general formula (1) having one or more hydrophilic groups per molecule and a metal element

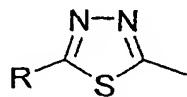


30

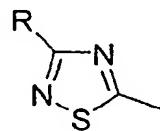
35

35

wherein  $X_1$  represents a chain of a plurality of atoms containing a total of 2 or more hetero atoms of one or more kinds selected from the group consisting of nitrogen atom, oxygen atom and sulfur atom and wherein  $X_1$  is required to form at least one 5- to 7-membered heterocyclic ring; the heterocyclic ring containing  $X_1$  may have substituents thereon; the substituents on the heterocyclic ring may further be condensed to form a condensed ring; the condensed heterocyclic ring containing  $X_1$  may be substituted, with the proviso that the heterocyclic ring containing  $X_1$  is not a heterocyclic ring represented by the following general formula (2) or (3); and  $Ar_1$  represents a naphthyl group represented by any one of the following general formulae (4) to (6):

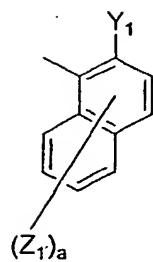
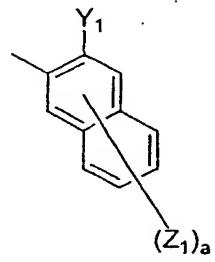
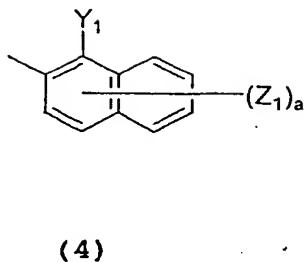


(2)



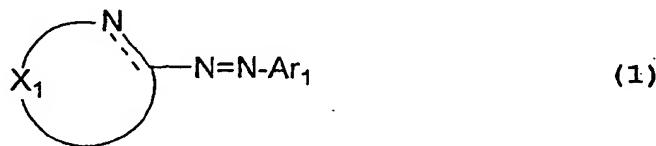
(3)

45 wherein R represents a hydrogen atom or an arbitrary substituent;

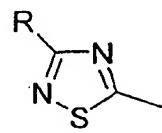
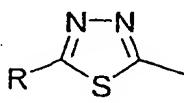


15 wherein  $Y_1$  represents a chelating group;  $Z_1$ 's represent arbitrary substituents which may be different from each other; and  $a$  represents an integer of from 0 to 6.

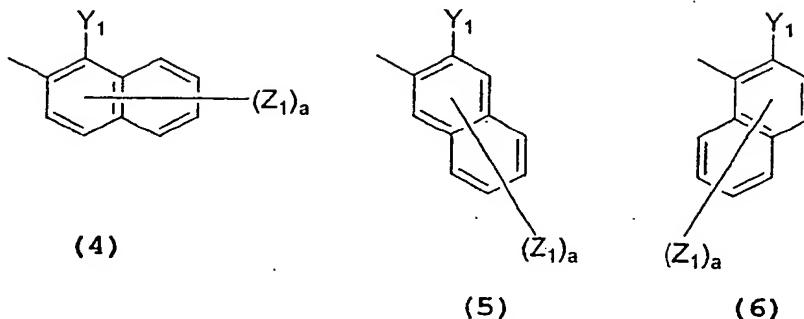
20 2. A metal chelated dyestuff for inkjet recording which is a water soluble azo metal chelated compound obtainable from an azo-based compound the free acid form of which is represented by the following general formula (1) and having one or more hydrophilic group per molecule and a metal element



10 wherein  $X_1$  represents a chain of a plurality of atoms containing a total of 2 or more hetero atoms of one or more kinds selected from the group consisting of nitrogen atom, oxygen atom and sulfur atom and wherein  $X_1$  is required to form at least one 5- to 7-membered heterocyclic ring; the heterocyclic ring containing  $X_1$  may have substituents thereon; the substituents on the heterocyclic ring may further be condensed to form a condensed ring; the condensed heterocyclic ring containing  $X_1$  may be substituted, with the proviso that the heterocyclic ring containing  $X_1$  is not a heterocyclic ring represented by the following general formula (2) or (3); and  $Ar_1$  represents a naphthyl group represented by any one of the following general formulae (4) to (6):



wherein  $R$  represents a hydrogen atom or an arbitrary substituent;



15 wherein  $Y_1$  represents a chelating group;  $Z_1$ 's represent arbitrary substituents which may be different from each other; and  $a$  represents an integer of from 0 to 6.

20

3. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the atom chain of  $X_1$  in the general formula (1) the atom adjacent to the carbon to which the azo group is connected is a nitrogen atom or oxygen atom.
4. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  is one selected from the group consisting of triazole ring, tetrazole ring, oxadiazole ring and thiadiazole ring which may have substituents.

25

5. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  has one or more substituents and the substituents on the heterocyclic ring each independently are a group selected from the group consisting of alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, allyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carbamoyl group which may be substituted, acyl group which may be substituted, carboxyl group, hydroxyl group, cyano group, amino group which may be substituted, acylamino group which may be substituted, nitro group, halogen atom, phosphono group, sulfo group, mercapto group, alkylthio group which may be substituted, alkylsulfonyl group which may be substituted, alkylsulfonyl group which may be substituted and thiocyanato group.

30

6. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the general formulae (4) to (6),  $Y_1$  is a hydroxyl group, carboxyl group, amino group which may be substituted, sulfo group, carbamoyl group, alkoxy group which may be substituted, alkylthio group which may be substituted, alkylsulfonylamino group which may be substituted or arylsulfonylamino group which may be substituted.

35

7. A metal chelated dyestuff for inkjet recording as defined in Claim 6, wherein in the general formulae (4) to (6),  $Y_1$  is hydroxyl group, alkoxy group which may be substituted or amino group which may be substituted.

40

8. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the general formulae (4) to (6), the  $Z_1$ 's each independently are a group selected from the group consisting of alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, carbamoyl group which may be substituted, carboxyanilide group which may be substituted, hydroxyl group, amino group which may be substituted, ureide group, acylamino group which may be substituted, alkylsulfonylamino group which may be substituted, arylsulfonylamino group which may be substituted, phosphono group, sulfo group and sulfamoyl group which may be substituted.

45

9. A metal chelated dyestuff for inkjet recording as defined in Claim 1 or 2, wherein in the general formula (1),  $Ar_1$  is represented by the general formula (6).

50

10. A metal chelated dyestuff for inkjet recording as defined in Claim 9, wherein in the general formula (6), if the carbon connected to the azo group is at the 1-position,  $Z_1$  is connected to the carbon at the 3-position.

11. A metal chelated dyestuff for inkjet recording as defined in Claim 10, wherein in the general formula (6),  $Z_1$  connected to the carbon at the 3-position is a sulfo group or sulfamoyl group which may be substituted.

5 12. A metal chelated dyestuff for inkjet recording as defined in Claim 4, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  is represented by the following general formula (7):



EP 1 270 676 A1

wherein  $R_3$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, carbamoyl group, hydroxyl group, cyano group or sulfo group.

5 15. A metal chelated dyestuff for inkjet recording as defined in Claim 4, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  is represented by the following general formula (9):



15 16. A metal chelated dyestuff for inkjet recording as defined in Claim 4, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  is represented by the following general formula (10):

wherein  $R_4$  represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group which may be substituted.

20 25 16. A metal chelated dyestuff for inkjet recording as defined in Claim 4, wherein in the general formula (1), the heterocyclic ring containing  $X_1$  is represented by the following general formula (10):



30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 9835 9840 9845 9850 9855 9860 9865 9870 9875 9880 9885 9890 9895 9900 9905 9910 9915 9920 9925 9930 9935 9940 9945 9950 9955 9960 9965 9970 9975 9980 9985 9990 9995 9999

EP 1 270 676 A1

dyestuff is a water soluble azo metal chelated dyestuff obtainable from the azo-based compound and copper element.

5 20. A metal chelated dyestuff for inkjet recording as defined in Claim 18, wherein the water soluble azo metal chelated dyestuff is a water soluble azo metal chelated dyestuff obtainable from the azo-based compound and nickel element.

10 21. An aqueous inkjet recording liquid comprising an aqueous medium and one or more metal chelated dyestuffs for inkjet recording as defined in Claim 1 or 2.

15 22. An inkjet recording method using an aqueous inkjet recording liquid as defined in Claim 21.

15

20

25

30

35

40

45

50



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 02 01 3629

DOCUMENTS CONSIDERED TO BE RELEVANT																		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)															
X	DATABASE WPI Section Ch, Week 197438 Derwent Publications Ltd., London, GB; Class A60, AN 1974-66767V XP002212999 -& JP 48 089932 A (HODOGAYA CHEM CO LTD), 24 November 1973 (1973-11-24) * abstract; examples 6,9 *	1-4, 6-11,18	C09B45/34 C09D11/02															
A	DE 651 105 C (I G FARBENINDUSTRIE AKT GES) 7 October 1937 (1937-10-07) * Dye 7 *	1-8,12																
A	EP 0 902 064 A (HEWLETT PACKARD CO) 17 March 1999 (1999-03-17) * the whole document *	1-22																
D	& JP 11 140367 A 25 May 1999 (1999-05-25) -----																	
A,D	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) -& JP 10 259331 A (KONICA CORP), 29 September 1998 (1998-09-29) * Compounds L14-L16, L30 * * abstract *	1-22																
P,A	WO 01 48090 A (CHINO TOMOHIRO ;YAMADA MASAHIRO (JP); YONEYAMA TOMIO (JP); MITSUBI) 5 July 2001 (2001-07-05) * table 4 * & JP 2002 080765 A 19 March 2002 (2002-03-19) -----	1-22																
D																		
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>12 September 2002</td> <td>Ginoux, C</td> </tr> <tr> <td colspan="3">CATEGORY OF CITED DOCUMENTS</td> </tr> <tr> <td colspan="3">           X : particularly relevant if taken alone            Y : particularly relevant if combined with another document of the same category            A : technological background            O : non-written disclosure            P : intermediate document         </td> </tr> <tr> <td colspan="3">           T : theory or principle underlying the invention            E : earlier patent document, but published on, or after the filing date            D : document cited in the application            L : document cited for other reasons            S : member of the same patent family, corresponding document         </td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	12 September 2002	Ginoux, C	CATEGORY OF CITED DOCUMENTS			X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document		
Place of search	Date of completion of the search	Examiner																
THE HAGUE	12 September 2002	Ginoux, C																
CATEGORY OF CITED DOCUMENTS																		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document																		
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document																		

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 02 01 3629

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-09-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
JP 48089932	A	24-11-1973	JP JP	833706 C 51007490 B	30-10-1976 08-03-1976
DE 651105	C	07-10-1937		NONE	
EP 0902064	A	17-03-1999	US EP JP	5980622 A 0902064 A1 11140367 A	09-11-1999 17-03-1999 25-05-1999
JP 10259331	A	29-09-1998		NONE	
WO 0148090	A	05-07-2001	WO JP	0148090 A1 2002080765 A	05-07-2001 19-03-2002

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**